Metal Science and Heat Treatment, Vol. 55, Nos. 5 – 6, September, 2013 (Russian Original Nos. 5 – 6, May – June, 2013)

UDC 669.35:669.15-194.55

CREATION OF COMPOSITE BRONZE – MARAGING STEEL ALLOY

B. A. Potekhin,[1] V. V. Ilyushin,[1] A. S. Khristolyubov,[1] A. Yu. Zhilyakov,[2] and A. Ernandes[3]

Translated from *Metallovedenie i Termicheskaya Obrabotka Metallov*, No. 5, pp. 6 – 10, May, 2013.

The possibility is demonstrated of creating alloys based on the system Cu – Fe – Ni – Al, within which the matrix is bronze BrNA 4-1, "reinforced" with dendrites containing, apart from Fe and Cu, about 15% Ni and 1% Al. This dendrite composition provides dispersion hardening. Favorable dendrite morphology provides high deformability of these bronzes, and makes it possible to control mechanical and service properties by heat treatment over a wide range.

Key words: bronze, maraging steel, combined alloy, morphology.

INTRODUCTION

A broad range of bronzes is due to the variety of fields of application. Tin bronzes, for example BRO10, is used extensively as a cast alloy, exhibiting good antifriction properties (BrO10F1) [1]. However, they do not deform either in cold or hot conditions due to unfavorable brittle intermetallic Cu_3Sn morphology (Fig. 1*a*). As a result the field of application of these bronzes is limited, i.e., solely manufacture of cast components; forming and welding them is impossible.

Dispersion-hardened bronzes of type BrAZhN 10-4-4 are used for friction assemblies [1], although they do not deform in a cold condition.

Other bronzes (BrA7, BrB2, BrBNT) exhibit a good set of properties, but are not intended for use in sliding friction assemblies.

Thus, there is interest in increasing the level of sliding alloy unification based on copper, i.e., preparation of bronzes with improved properties and production characteristics, and they could replace well-known alloys, for example BrO10F1, BrAZhN 10-4-4, etc. [1].

The aim of this work is creation of composite material with a set of satisfactory production, mechanical, and high service properties (low friction coefficient, high wear resistance) based on bronze reinforced with maraging steel dendrites.

METHODS OF STUDY

On the basis of analyzing the diagrams Cu – Fe, Cu – Co, Cu – Ni, Fe – Ni, Fe – Al, Cu – Al [2] composite material compositions have been calculated (subsequently experimental bronzes) with a matrix of bronze type BrNA 4-1 and hard inclusions of maraging steel type 03N15Yu1. The chemical composition of these bronzes is presented in Table 1.

Ingots of test bronzes weighing 0.5 and 1.0 kg were prepared by melting pure charge materials in a Tamman melting furnace in alundum crucibles in a reducing carbon dioxide CO atmosphere.

Metallographic studies were carried out using a light (Carl Zeiss AxioObserver A1m and scanning electron (Carl Zeiss EV050) microscopes.

General and local chemical analyses were performed in a JEOL JSM 6490-LV scanning electron microscope with an attachment for microanalysis Oxford Inca DryCool (resolution 133 eV).[4]

Heat treatment of test bronzes was carried in a SNOL 8.2/1100 chamber furnace and the temperature did not deviate from that prescribed by ±5°C.

[4] The study was performed in the laboratory of structural methods of analysis and properties of materials and nanomaterials of TsKP UrFU under the direction of S. V. Belikov.

TABLE 1. Experimental Bronze Chemical Composition

Bronze	Element content,* wt.%		
	Fe	Ni	Al
BrZhN 12-6	12.20	5.94	–
BrZhNA 12-6-1	12.88	5.98	1.04
BrZhNA 12-7-1.5	12.29	7.56	1.49

* Balance — copper.

Note. Total amount of impurities did not exceed 0.12 wt.%.

[1] Ural State Polytechnic University, Ekaterinburg, Russia.
[2] B. N. El'tsin Ural Federal University (UrFU), Ekaterinburg, Russia.
[3] Universidad de Cienfuegos "Carlos Rafael Rodroguez", Cinefuegos, Cuba (e-mail: pba-nn@yandex.ru).

Microhardness of structural components of cast and heat treated alloys was measured in PMT-3 and 402MVD instruments in accordance with GOST 9450–76 with a load range 0.02 – 0.05 kg.

Deformability was measured by bending wedge-shaped specimens over a mandrel with radius 100 mm (Fig. 2*a*). Deformation development was observed in a polished surface: simultaneously in tension over the outer radius and compression over the inner radius (Fig. 2*b*).

Alloy mechanical properties were determined[4] in tensile tests of standard fivefold specimens with a gage length diameter of 5 mm at room temperature in an Instron 3382 machine.

Friction coefficient and wear intensity were evaluated in a special device mounted on the base of a lathe with NPC. Testing was carried out by a disk–finger specimen scheme with continuous computer recording of test parameters (pressure, sliding rate, temperature, etc.). In each test case there were three specimens with a size of $6 \times 6 \times 12$ mm; the counterbody was a disk of steel ShKh15 (45 *HRC*). The test procedure has been described in [3].

RESULTS AND DISCUSSION

Iron and cobalt have unlimited solubility in copper in a liquid condition, and little solubility in the solid state: solubility of Fe in Cu at 950°C is 1.92 wt.%; at 800°C it is 1.02 wt.%; at 60°C it is less 0.05 wt.% [2].

According to data in [2] test bronzes (Table 1) solidify at a temperature of about 1200°C, with which formation of Fe – Ni dendrites commences.

Nickel, although it forms of series continuous solid solutions in the Cu – Ni system, has greater chemical affinity for iron than for copper. In view of this during solidification and cooling Ni together with Fe forms a dendrite-like structure. The main mass of iron in experimental bronzes is within dendrite-like precipitates of round shape (Figs. 1*b* and 3).

Aluminum during solidification is redistributed so that within the matrix its content is about 1.5%, and in precipitates it is about 0.8% (Table 2).

Within the central part of a precipitate (Fig. 3) there is a "pearlite-like" structure, which according to local chemical analysis data consists of layers of solid solutions type N15 (Fe + 15% Ni) and α (Cu + 25% Ni). This part of a dendrite formed during solidification. Over the edges of such a precipitate the structure is monolithic and formed in the cooling stage for solidifying alloy. This structure indicates that with a reduction in temperature from 1000 to 600°C Fe and Ni atoms diffuse from the matrix in the direction of already forming dendrites.

Matrix at a distance of 60 μm or more from an inclusions contains 3 – 4% Fe and 4 – 5% Ni. At a distance up to 20 μm the amount of iron and nickel increases to 10 and 6.5% respectively. Apart from relatively massive dendrite-like precipitates with a size up to 100 mm within a matrix of compo-

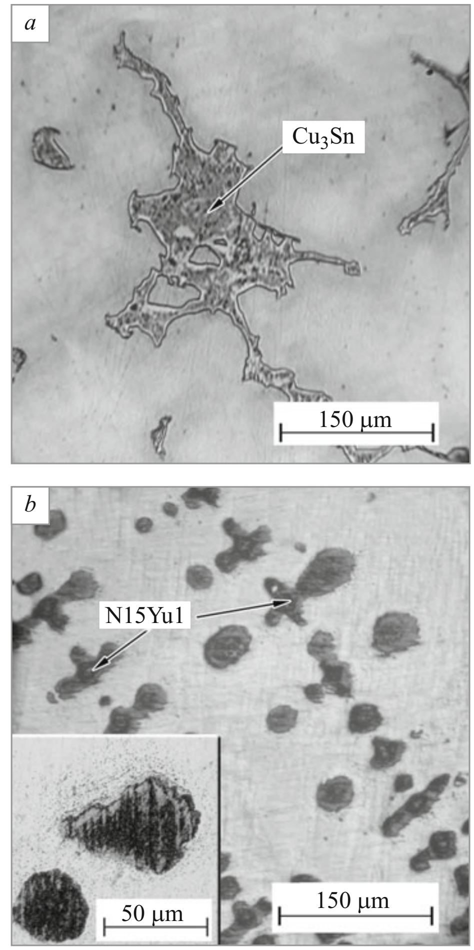

Fig. 1. Microstructure of bronzes BrO10 (*a*) and BrZhNA 12-6-1 (*b*).

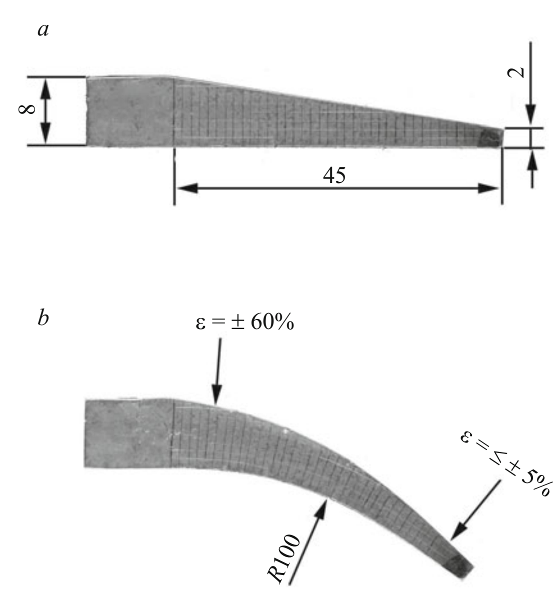

Fig. 2. Scheme for determining bronze deformability in bending (tension – compression): *a*) specimen before deformation; *b*) after deformation by bending at 20°C.

TABLE 2. Alloying Element Redistribution After Different Heat Treatment of Experimental Bronzes

Heat treatment	Zone*	Element content, wt.%							
		Fe	Ni	Al	Cu	Fe	Ni	Al	Cu
		Bronze BrZhNA 12-6-1				Bronze BrZhNA 12-7-1.5			
Cast condition	*1*	2.5	4.1	1.4	91.9	6.8	6.6	1.5	85.1
	2	10.6	7.8	1.2	80.3	7.1	7.2	1.6	84.7
	3	12.0	8.6	0.9	78.4	7.8	6.7	1.8	83.7
	4	11.3	7.1	1.0	80.6	31.2	12.0	1.5	55.3
	5	58.4	15.2	0.6	25.7	58.1	17.6	1.4	22.9
Hardening	*1*	3.3	3.5	0.9	92.5	3.0	3.8	1.7	91.5
	2	6.0	5.2	1.0	87.7	5.1	5.8	1.7	83.4
	3	9.9	6.5	0.9	82.7	9.8	7.9	1.8	80.5
	4	27.1	11.8	0.9	60.1	29.0	11.6	1.9	64.5
	5	60.1	15.8	0.6	23.4	58.0	16.5	1.5	24.0
Hardening + aging	*1*	3.1	3.6	0.9	92.3	3.4	4.3	1.5	90.8
	2	5.3	4.6	1.1	88.9	3.7	4.8	1.4	90.1
	3	6.1	5.1	1.0	87.7	5.9	5.7	1.6	86.8
	4	5.0	4.8	1.4	88.7	9.3	7.3	1.6	81.8
	5	61.6	14.7	0.8	22.8	59.0	17.7	1.5	21.8

* See Fig. 3*b*.

Note. Hardening regime is holding at 950°C for 1 h, water cooling, aging regime is 450°C for 2 h.

sition 4 – 6 % Ni, 1.5% Al (balance copper) there are fine inclusions of Fe – Ni – Al, which form as a result in a reduction of Fe and Cu solubility with a reduction in temperature to 600°C.

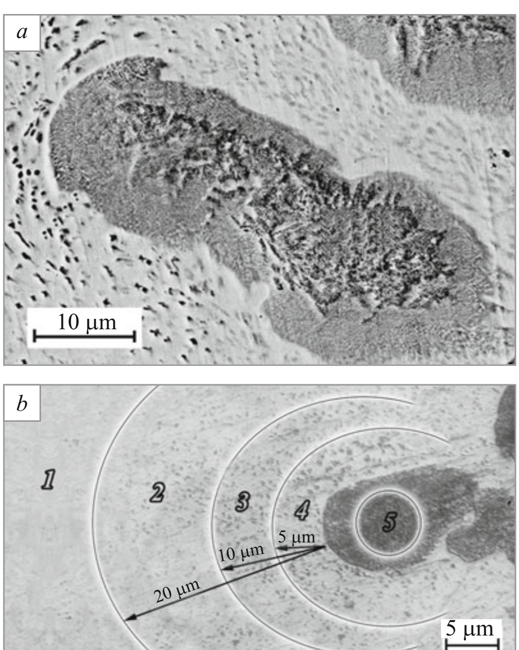

Fig. 3. Structure of precipitates (*a*) and area location scheme (*b*) in bronze BrZhNA 12-6-1.

It may be suggested that these fine Fe – Ni inclusions formed in the last solidification stage, and their average size (in a microsection plane) does not exceed 0.1 µm, but close to a dendrite it reaches 1 µm. This difference in fine inclusion size is apparently due to their directional movement towards “massive” inclusions in the solid state in the temperature range where there is still sufficient Fe solubility in Cu. At lower temperature (≤ 500°C) only nickel diffusion into iron inclusions is possible. It is not excluded however that Fe – Ni “clusters” may diffuse into copper at lower temperature.

Test bronzes (Table 1) differ insignificantly with respect to chemical composition and structure. With heating to 950°C with soaking for 1 h the distribution of alloying elements between matrix and dendrites is similar (Table 2). In view of this results are provided below solely for a study of bronze BrZhNA 12-6-1.

Microhardness of structural components, having a dendritic structure, is quite high, i.e., 410 HV_{50}. This is due to the fact that within the Fe – Ni – Al system during solidification and cooling there is formation of intermetallics FeNi and Fe_3Ni, and also possibly FeAl [2].

Heating of ingots to 950°C with soaking for 1 h and “fixing” by water quenching indicates that dendrites continue to be enriched with iron (Table 2) due to dissolution of fine “matrix” precipitates. The microhardness of all structural components of bronze changes markedly (Table 3).

TABLE 3. Microhardness of Bronze BrZhNA 12-6-1 after Heat Treatment

Zone*	Microhardness HV, kgf/mm^2		
	Without HT	Hardening	Hardening + aging
1	170	106	109
3	165	125	129
5	410	203	335

* See Fig. 3*b*.

Note. Hardening from 950°C in water, aging at 450°C for 2 h.

The hardness of matrix after quenching decreases as a result of "joining" of fine matrix Fe – Ni precipitates to dendrites, and the hardness of dendrites increases a result of dissolution within them of FeNi and FeAl type intermetallics. Subsequent aging forms in Fe – Ni dendrites other intermetallics (NiAl, Ni_3Al), and therefore their microhardness increases considerably. Thus, with stagewise heat treatment by a scheme: ingot $\rightarrow$ quenching $\rightarrow$ quenching + aging within dendrites there are the following processes respectively:

α-solid solution Fe – Ni – Al (in ingot) $\rightarrow$ α (after quenching) $\rightarrow$ α + NiAl, Ni_3Al (after aging)

Changes in hardness as a result of heat treatment are due mainly to diffusion of Fe and Ni in a direction of already existing inclusions, particularly in the soaking period for specimens for quenching at 950°C for 1 h. There is a change in chemical composition of both matrix and inclusions. Redistribution of alloying elements in alloy BrZhNA 12-6-1 between structural components as a result of heating at 950°C is recorded by quenching and subsequent aging at 450°C for 2 h, presented in Table 2. Based on data [3] and results obtained (Table 2) it might be proposed that in the Cu – Fe – Ni system in question the chemical affinity of Ni for Fe is greater than the affinity of Ni for Cu. This predetermines diffusion of Ni from the matrix into dendrites during solidification and subsequent heat treatment.

Aging of quenched alloy does not affect matrix hardness, but the hardness of dendrites increases (Table 3). Within dendrites during aging of martensite formed during quenching, similar in composition to Fe – 15% Ni – 0.6% Al, there is formation of intermetallics type Ni_3Al, NiAl, which also provides strengthening.

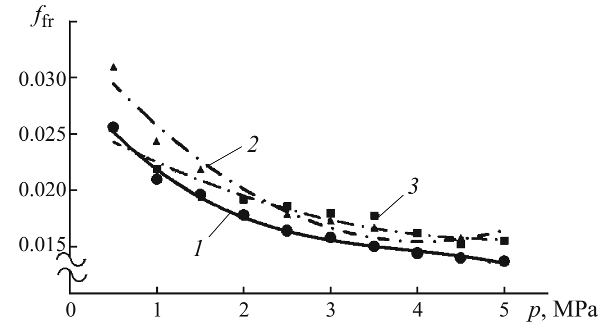

Fig. 4. Dependence of friction coefficient f_{fr} on pressure p during bronze friction testing: *1*) BrO10 in cast condition, wear intensity $I = 0.025$; *2*) BrZhNA 12-6-1 in cast condition, $I = 0.045$; *3*) BrZhNA 12-6-1 after hardening from 950°C (1 h) in water and aging at 450°C, 2 h, $I = 0.032$.

Control alloy BrZhNA 12-6 was studied (Table 1), differing from alloy BrZhNA 12-6-1 solely by absence of aluminum. It was established that aluminum does not have any marked effect on structure morphology and chemical redistribution of Fe and Ni in the alloy. Aging of dendrites at 450°C does not proceed in the alloy, since NiAl and Ni_3Al intermetallics simply do not form from it in the absence of Al. Thus, presence of aluminum in an amount of 1.0 – 1.5% within bronze BrZhNA 12-6-1 is necessary in order to control alloy properties.

Results of friction tests with a sliding rate of 3.5 m/sec are provided in Fig. 4. It is seen that the friction coefficient for bronze BrZhNA 12-6-1 almost equal that for basic material, i.e., bronze BrO10 in the test range of loads and rates.

Mechanical test results are given in Table 4 for bronze BrZhNA 12-6-1 after heat treatment, and for comparison bronze BrO10.

Previous laboratory tests have also shown that bronze BrZhNA 12-6-1 has high ductility in bending at room temperature (cracks were not observed with bending up to 60%) and deform well in a hot condition. Thus, it is possible to manufacture castings, rolled product, and welded joints.

CONCLUSIONS

Bronze BrZhNA 12-6-1 is proposed as an alternative to standard bronze BrO10, being a composite material within which the copper matrix (bronze BrNA 4-1) is reinforced with dendrites. This material differs fundamentally from

TABLE 4. Mechanical Properties of Experimental Bronze BrZhNA 12-6-1 and Standard Bronze BrO10 [1]

Bronze	Heat treatment regime	σ_r, MPa	$\sigma_{0.2}$, MPa	δ, %	ψ, %
BrZhNA 12-6-1	Without HT	364	170	38	43
	Hardening from 950°C (1 h) in water	300	147	67	–
	Hardening + aging at 450°C, 2 h	301	149	51	39
BrO10	Without HT	215	175	3 – 10	10 – 14

bronze in the fact that instead of brittle intermetallic Cu_3Sn, it contains dendrites corresponding to the composition of maraging steel N15Yu1, These dendrites, in contrast to intermetallic Cu_3Sn, deform in cold and hot conditions, as for typical maraging steel. A composite alloy of this type, in contrast to bronze BrO10, may be used not only in a cast condition, but also in a deformed condition in the form of rolled product and forgings. Its tribological properties are no worse than bronze BrO10, and ductility is much higher.

REFERENCES

1. B. N. Arzamasov, V. A. Brostem, N. A. Bushe, et al., *Structural Materials: Handbook* [in Russian], Mashinostroenie, Moscow (1990).
2. *Binary Metal System Composition Diagrams: Handbook, Vol. 2* [in Russian], Mashinostroenie, Moscow (1997).
3. B. A. Potekhin, V. V. Ilyushin, and A. S. Khristolyubov, “Special properties of babbit B83 prepared by a turbulent casting method,” *Lit’e Metall*., No. 3(57), 78 – 81 (2010).